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The Electrolytic Determination of Manganese and Its Separation from Zinc and Iron.

THESIS.

Presented to the Faculty of the Department of Philosophy of the University of Pennsylvania in Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy,

BY

GEORGE PHILIPP SCHOLL,

Philadelphia.

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THE ELECTROLYTIC DETERMINATION OF MANGANESE AND ITS SEPARATION FROM ZINC AND IRON.

The deposition of manganese during electrolysis takes place in a different manner from that of the other metals, with the exception of lead, inasmuch as under ordinary conditions the metal is not deposited as such on the kathode, but comes down as peroxide on the anode. Under certain conditions it is, however, possible to deposit the metal as such on the kathode,[1] but its quantitative estimation has been found impossible on account of the very rapid oxidation of the metal during the process of drying. This method therefore cannot be used for analytical purposes.

The deposition of manganese as peroxide for the purpose of its quantitative chemical estimation by electrolysis has been the subject of a good deal of investigation,[2] but the results have not been very satisfactory. The stumbling block in the way of a successful precipitation has been the fact, that it is extremely difficult to obtain the deposit on the anode in an adherent form, it showing a tendency to become loose and to scale off. This even takes place when the peroxide is deposited on a platinum dish, the inner surface of which has been roughened by subjecting it to the action of a sand-blast. Owing to this tendency, manganese is probably the most difficult metal to deal with, as far as electrolysis is concerned.

Various electrolytes have been proposed for the quantitative estimation of manganese by electrolysis, but in 1894 Classen[3] states, that none of the methods heretofore proposed had been found by him to yield satisfactory results. He advises the use of acetic acid as an electrolyte and states that it has been found by him to be the most suitable of all the organic acids. This statement is repeated in the last (4th edition) of his "Quantitative Chemical Analysis by Electrolysis," translated by Herrick and Boltwood, 1898, p. 149, where it is further said, that "the precipitation of large quantities,

[1] Smith and Frankel: Journal Analyt. Chem., **3**, 385; Chemical News, **60**, 262.

[2] Literature given by Smith, Electrochemical Analysis, 3rd ed., 1902; Riché: Annales de Chimie et de Physique [5th series], **13**, 508; Luckow: Zeitsch. f. anal. Chem., **19**, 17; Schucht; Zeitsch. f. anal. Chem., **22**, 493; Classen and von Reiss: Berichte deutsch. Chem. Ges., **14**, 1622; Brant: Zeitsch. f. anal. Chem., **28**, 581; Rüdorff; Zeitsch. f. angew. Chem., **15**, 6; Classen: Berichte deutsch chem. Ges., **27**, 2060; Engels: Zeitsch. f. Electrochemie, **2**, 413; **3**, 286; Groeger: Zeitsch. f. angew. Chem., 1895, p. 253; Koeppel: Zeitsch. f. anorgan. Chem., **16**, 268.

[3] Berichte d. deutsch. Chem. Ges., **27**, 2060.

even when roughened dishes are used, cannot be successfully carried out, since it is impossible to obtain firmly adherent precipitates." Evidently no improvement in this method had been made up to 1901, for in Classen's large handbook on "Selected Methods of Analytical Chemistry," which appeared in that year, the following statement is found on page 368: "In acetic acid solution it is only possible to deposit quantities of about 0.08 gram of manganese in the form of peroxide, even on roughened dishes."

A few years ago, Engels[1] proposed a method, which is said to give firmly adherent deposits up to 0.25 gram of manganese, and which consisted in adding chrome alum in quantities of from 1.5 to 2 grams to the solution of manganese sulphate. This method is open to objection, inasmuch as the addition of chrome alum introduces a complex metallic compound into the electrolyte, which compound by its own decomposition under the influence of the current may give rise to complications. Further, as stated by Kaeppel,[2] an extended washing of the deposit, on account of the chromic acid adhering to it, is absolutely necessary, and a source of error may easily be introduced from the fact, that chromic acid, which is carried down by the deposit, is quite firmly held by the peroxide of maganese.

The last work done on the subject in recent years has been by Kaeppel, who in 1898 published a method[2] by which, according to him, very adherent deposits of manganese peroxide are obtained. It consists in the addition of acetone, in quantities varying from 2.5 to 10 cc., to a solution of manganese sulphate. He gives one experiment, in which he obtained 1.61 grams of peroxide of manganese in a firmly adherent form. Classen[3] states, however, that the carrying out of Kaeppel's method in his laboratory has not led to any satisfactory result.

The question of the deposition of manganese was therefore, as is apparent from the above, in quite an unsatisfactory state. Engels's method was open to the objections mentioned, and Kaeppel's method was described by him in such a way in his publication, that it was impossible to repeat it. As has been justly criticized by Classen,[4] he omitted to state the precise conditions, under which his experiments were performed. He gives no data

[1] Zeitsch. f. Electrochemie, **2**, 413; **3**, 286.
[2] Zeitsch. f. anorgan. Chemie, **16**, 268.
[3] Selected Methods of Analytical Chemistry, 1901, p. 370.
[4] Ausgewählte Methoden der analytischen Chemie (selected methods, etc.), p. 370.

whatever in regard to the size and form of his electrodes, the current density at the anode and kathode or the general arrangement for carrying out the electrolysis. It is quite apparent to any one conversant with electrolytic operations in general, that these are questions, which largely influence the result, and on which the success of the operation may depend and usually does depend to no small degree.[1] Such being the case, the question presented itself, if it was not possible to find another electrolyte, which would lend itself to a more satisfactory deposition of the peroxide of manganese, and to the separation of manganese from other metals, principally iron. Organc acids appeared most suitable for this purpose. Classen[2] maintains, that strong inorganic acids interfere with the deposit and even make it impossible. The same author's statement, that acetic acid is the best of all organic acids, has been referred to above. No further experimental details are given in his publications to substantiate that statement and there is also no mention made as to which organic acids have been tried and under what conditions. Kaeppel, in his paper, makes some remarks about formic acid. He says: "I then carried out experiments with formic acid. By the use of a few drops of it, an adherent deposit could also be obtained, but it was shown still more, that a quantitative deposition could not be effected. The addition of more than 5 drops of the acid prevented the deposition of peroxide altogether. This statement is also unaccompanied by any experimental evidence as to the strength of acid used, the manner of carrying out the electrolysis and the general conditions under which it took place.

The above statements to the contrary notwithstanding, it was considered, that formic acid, on account of its simple constitution, would be an extremely desirable substance to be used as electrolyte, and it was thought, that under the right conditions it might be made to yield satisfactory results. It was therefore determined to try it with the addition of sodium formate.

The apparatus used for carrying out the experiments, consisted of the usual stand for electrolysis, provided with a glass rod carrying a ring wih 3 contact points, for the purpose of supporting the platinum dishes in which the deposition took place, and the

[1] See in this connection the pertinent remarks of Smith :Electrochemical Analysis 3rd ed., p. 33-36.

[2] *Ibid.*, p. 368. Quantitative Analysis by Electrolysis, p. 149.

usual clamp for fastening the other electrode. The current was supplied by storage batteries, which were constantly kept in a charged condition. The current was regulated by means of a disk rheostat, and a Weston voltmeter and amperemeter were kept constantly in the circuit. The platinum dishes used for the deposition of the peroxide of manganese were of the usual shape and had a diameter of 9 cm. Their interior surface was roughened. The kathode consisted of a spiral of platinum wire of 1½ mm. diameter, having a surface of 6 square cm. As usual, the dishes were covered by cover glasses.

A solution of manganese sulphate was made up, calculated to contain about 10.60 grams of manganese in the liter. The formic acid used in the experiments was the chemically-pure article of 1.06 specific gravity, made by Merck & Co. The electrolysis was conducted in the following manner: 10 cc. of the manganese sulphate solution were introduced into the platinum dish and 5 cc. of the formic acid solution of 1.06 specific gravity added to it. A solution of 10 cc. of sodium formate, containing 1 gram of the salt, was then added, and the whole volume of the solution made up with distilled water to about 130 cc., so that it covered, as accurately as could be determined, 100 sq. cm. of the surface of the dish. The dish was connected as anode and the spiral kathode introduced into the solution, care being taken to arrange it as nearly as possible equidistant from the sides and the bottom of the dish, in order to obtain as uniform a distribution of the current as possible. It was considered best to use a high current density, as most suitable for the deposition of the peroxide. The current was therefore regulated to give a strength of 1.4 amperes, which was maintained during electrolysis. The pressure between the electrodes was 12 volts at the beginning, decreasing to 8.6 volts at the end. Almost immediately after the circuit had been closed, a deep black, shining deposit appeared at the anode. The current was allowed to act for one and one-half hours, when the level of the liquid was raised to ascertain whether any more peroxide would precipitate. As no further precipitation took place, the liquid was siphoned off and replaced by water, without interrupting the current. The deposit showed a deep black, shining color and was firmly adherent to the dish, showing no tendency to come off during washing. It was washed carefully with water

and dried. Smith[1] states that it is useless to try to obtain a definite compound by drying the deposit, as it is so extremely hygroscopic, that ignition alone to the protosesquioxide will give definite and concordant results. This was found to be true. Though the precipitate looked very well and had quite a metallic appearance, it was not possible to get a concordant weight, as it attracted moisture very rapidly. Following the directions given by Smith (l.c.) the deposit was ignited over the Bunsen burner and the blast lamp, and thus changed to the protosesquioxide, when it could be weighed without any trouble. The solution, when tested, failed to show the presence of manganese. The following table shows the results of four determinations made in exactly the same manner:

Electrolyte.	Time.	Temperature.	N.D.$_{100}$ at anode.	Voltage.	Mn found. Grams.
10 cc. $MnSO_4$ + 5 cc. HCOOH 1.06 sp. gr. + 10 cc. = 1 gm. sodium formate.	$1^1/_2$ hrs.	Ordinary temp. at start, heated up by action of current to 40°–50° at the end.	1.4	12.0 volts at start to 8.6 volts at end.	0.1100 0.1105 0.1104 0.1101

It was thus established that Kaeppel's statement, that more than five drops of formic acid entirely prevented the formation of peroxide of manganese, did not hold true under the conditions under which the experiments were run. It was further proved that it was very well possible to deposit the whole of the manganese in the presence of formic acid, even if the acid was present in amounts considerably above that given by Kaeppel as the maximum. According to Classen,[2] it is necessary in the carrying out of Engels's method, to weigh the platinum dish after the deposit of peroxide has been removed from it, as the dish suffers a diminution of weight during electrolysis, amounting to about 1 mg. With the electrolyte used in the experiments under consideration this does not take place, the dish losing either no weight at all or at the most only $^1/_{10}$ mg.

Though it was evident from the results tabulated above that concordant results could be obtained in this way by exactly duplicating the experiments, yet the results obtained were too high. It was also observed that even a prolonged ignition over the blast lamp failed to remove the hygroscopic character of the deposit entirely. Though the deposit could be weighed without any difficulty, it

[1] Electrochemical Analysis, 3rd ed., p. 96.

[2] Ausgewählte Methoden, p. 369.

continued to slowly attract moisture, and when standing over night, had gained perceptibly in weight.

Experiments were then conducted with a low voltage, so as to study the effect of a lower current and consequently lower current density on the deposit. The character of the deposit, however, remained unchanged, the lower currents, of course, requiring a proportionately longer time to effect the complete deposition of the manganese. Heating up of the electrolyte, to about 50° or 55°, had no accelerating effect, but it was in so far harmful, as it tended to make the deposit blistery and was inclined to scale off. It was then tried to see whether larger quantities of sodium formate would have a beneficial effect. It was, however, ascertained that larger quantities of that salt had a decidedly retardent effect. If it was present in quantities of 2½ grams the deposition was not complete in less than two and one-half hours. An interesting fact was revealed by the results, which are tabulated below.

Manganese sulphate.	Formic acid. 1.06 sp. g.	Sodium formate. Grams.	Time.	Temp.	$N.D_{100}$.	Voltage.	Mn found.
10	5	1	over night	ordinary	0.18	3.0	0.1131
10	5	1	4	"	0.21	4.0	0.1121
10	5	1	3	"	0.45	5.0	0.1108
10	5	2	2	"	1.0	4.5	0.1154
10	5	2½	2½	"	1.0	3.9	0.1180
10	5	2½	2½	"	1.0	3.9	0.1172

It will be noted that the amount of manganese found did not agree at all with the amount found in the experiments tabulated before. The amount of sodium formate present, as well as the time necessary for the electrolysis were both shown to have an influence on the result, the weight of the deposit increasing with the longer time and the larger amount of sodium formate. The hygroscopic nature of the deposits obtained was very evident, it being hardly possible to weigh those gotten when 2½ grams of sodium formate were present, even after they had been ignited over the blast lamp. The most reasonable explanation of this fact seemed to be that the sodium formate was also partly decomposed under the influence of the current, with the formation of caustic soda at the kathode. Some of this caustic soda, being specifically heavier than the electrolyte, falling down to the bottom of the dish anode, might easily have been enclosed

and held mechanically by the depositing peroxide of manganese. When the precipitation was slower, the same amount of sodium formate being present, the deposit had more time to seize upon and enclose alkali, hence the greater weight of the precipitate, the longer electrolysis was continued. On the other hand, when much formate was present, a greater amount of it would be decomposed and considerably more alkali could get into the deposit.

It should be noted in this connection that careless washing of the precipitated peroxide was entirely excluded, as everyone of the deposits was treated exactly alike. Whether the above explanation is the correct one has not been ascertained, as it was shown very soon by the following experiments that good results could be obtained without the use of sodium formate. That it is a perfectly rational one, in view of the results shown above and of the hygroscopic character of the deposit, even after ignition, can hardly be doubted. The tendency of the caustic alkali solution, which is produced during electrolysis, to fall down to the bottom of the vessel, is quite well known, as is also the fact that even in ordinary quantitative analysis it is a most difficult thing to get a precipitate free from alkali.

It was thus established that, though perfectly concordant results could be obtained by using formic acid with the addition of sodium formate, by adhering exactly to the same conditions, yet the results contained a source of error, which would make them practically worthless. However, the good results obtained so far with formic acid had raised quite a doubt as to the accuracy of Kaeppel's statement with regard to formic acid preventing the deposition of peroxide of manganese.

The next step was, consequently, to do away with the source of error traceable to the addition of sodium formate and to try formic acid alone. Accordingly, 10 cc. of the manganese sulphate solution were taken, 5 cc. of formic acid of 1.06 specific gravity added, and the solution subjected to electrolysis in the usual manner. The voltage required was pretty high, on account of the low conductivity of the formic acid, it being 17.5 volts between the electrodes at the start, with a current strength of 1 ampere. As the solution got very warm in about an hour, by the passage of the current, the voltage was decreased to 7.9 volts, giving an amperage of 0.8. The deposit did not come down as quickly as when sodium formate was present, but the manganese was all

out after four hours. The heating of the electrolyte, as had been ascertained before, did not have a favorable influence, tending to make the deposit blistery. The deposited peroxide of manganese was washed carefully and ignited in the usual way. The weight of the deposit, calculated as Mn, was 0.1063 gram, a value which closely agreed with that calculated to be present. It was further found that the precipitate was absolutely non-hygroscopic after ignition, and could be weighed with perfect ease. It was left purposely exposed to the action of the atmosphere over night and reweighed on the following morning, when the weight was found to be the same. The appearance of the deposit was the same as that obtained before. Kaeppel[1] contends that it is possible to weigh the deposit after drying for about two hours at 150° to 180°, thus doing away with the necessity of changing it to the protosesquioxide by ignition. This was tried, but Kaeppel's observation could not be confirmed, as the deposit attracted moisture too quickly to make it possible to obtain reliable results.

Another solution of manganese sulphate was then made up, and the manganese determined gravimetrically as pyrophosphate. There was 0.1034 gram of Mn found present in 10 cc. As the determinations with employment of the spiral of platinum wire as kathode had necessitated such a high potential between the electrodes in order to obtain the necessary strength of current and had thereby caused objectionable heating-up of the electrolyte, it was decided to adopt some means to get along with as low a voltage as possible, which would give the necessary current.

This could, of course, only be accomplished by reducing the resistance of the electrolyte, either by increasing its conductivity by the addition of a better conducting material, or by increasing the electrode surface. As the former course was intended to be avoided, the latter presented itself as the only solution. Accordingly, a so-called basket electrode was used, being a platinum dish, which conformed in shape to the interior surface of the roughened dish on which the precipitation of peroxide of manganese took place. It had a surface of 60 sq. cm. and was perforated with holes to allow of a better egress of the gases set free during electrolysis and a better mixing of the solution. The following table gives the results of some experiments carried out with varying quantities of formic acid and varying quantities of manganese.

[1] Loc. cit., p. 274.

Manganese taken.	Manganese found.	Formic acid. 1.09 sp. g.	Time.	Temp.	$N.D_{100}^{\blacksquare}$	Voltage.	Character of deposit.
0.1034	0.1036	5	2½	ordinary, rising toward the end.	0.8 to 1.0	7.6 at end.	satisfactory, adherent
0.1034	0.1034	5	"	"	"	"	"
0.1034	0.1034	5	"	"	"	"	"
0.1034	0.1035	5	"	"	"	"	"
0.1034	0.1033	5	"	"	"	"	"
0.1034	0.1035	10	3½	"	"	7.2	"
0.1034	0.1034	10	"	"	"	"	"
0.1034	0.1032	15	5	"	"	7.0	"
0.1551	0.1551	5	3¾	"	"	7.3	"
0.1551	0.1552	5	"	"	"	"	"
0.1551	0.1550	7½	4	"	"	7.0	"
0.1551	0.1449	10	5	"	"	6.8	"
0.2068	0.2069	5	5	"	"	6.6	" a trifle loose on washing.
0.2068	0.2069	5	5	"	"	"	" "
0.2068	0.2070	10	6¾	"	"	5.6	" "
0.2068	0.2071	10	"	"	"	"	" "
0.2068	0.2071	15	7	"	"	5.4	" "

As will be seen from the above table, the results obtained by electrolysis agree very closely with the gravimetric. For some reason, which has not been further investigated, the addition of sodium formate appears to have a tendency to accelerate the deposition, as the metal was out of the solution in one and one-half hours when sodium formate was present, while it took two and one-half hours for the formic acid alone. The deposits obtained were all very fine and beautifully adherent, only with 0.2880 gram of Mn_3O_4 a slight disposition towards loosening was noticeable. It was very slight however, and, owing to the scaly nature of the material it was quite easy to filter it out quickly on a small filter, wash, dry and remove it from the filter and add it to the bulk of the material in the dish, together with the ashes of the filter paper.

It is also apparent from the above table that the addition of more than 5 cc. of formic acid of 1.06 specific gravity has no beneficial effect. On the contrary, larger amounts of formic acid tend to retard the precipitation. Much less than 5 cc. of formic acid cannot be used, as there is a tendency to form flakes of a brown precipitate around the kathode, which has to be brought into solution again by the addition of more formic acid.

Other experiments were run with a view of establishing whether the addition of ammonium formate would have any accelerating or otherwise beneficial effect on the deposit. Such was not found to be the case. When ammonium formate was present in small amounts, no better quality of the deposit could be obtained than could be gotten when it was not present. There was then also no decided effect upon the time of precipitation, the time in all cases being about the same as in the experiments run without sodium formate, or being slightly in favor of the latter. If, however, more ammonium formate was added, the quantity of manganese sulphate and formic acid remaining the same, it was quite apparent that a great retardation in the time of deposition took place and a very decided change for the worse in the character of the deposit. It will be noticed in the following table, for instance, that the complete deposition of the manganese was obtained in one case where 0.1034 of Mn were present as sulphate, and 5 cc. of formic acid, in two and one-half hours. The deposit obtained in this case was very satisfactory. The addition of 2 cc. of ammonium formate to this electrolyte retarded the time of

complete deposition to four and one-half hours, and the deposit obtained came off the dish to a considerable extent. The same same thing happened when 4 cc. of ammonium formate were added to an electrolyte, which had given satisfactory results with 2 cc. of the salt. The ammonium formate was produced by neutralizing the 1.06 specific gravity acid with ammonia.

Mn present.	Mn found.	Formic acid 1.06 sp. gr. cc.	Ammonium formate. cc.	Time hours.	Temp.	$N.D._{100}$.	Voltage.	Character of deposit.
0.1034	0.1034	5	..	$2\frac{1}{2}$	ordinary	0.8 to 1.0	7.6	good
0.1034	0.1036	5	2	$4\frac{1}{2}$	"	0.8	5.0	bad
0.1551	0.1552	5	2	$3\frac{3}{4}$	"	0.8	5.2	good
0.1551	0.1551	5	2	12	"	0.25	3.0	good
0.1551	0.1547	5	4	7	"	0.8	4.2	very bad
0.1551	0.1552	8	2	4	"	0.8	5.0	good
0.1551	0.1550	10	2	5	"	0.8	4.8	good

It was further tried whether the addition of chrome alum, as recommended by Engels, would have a beneficial effect when added to a formic acid electrolyte. The electrolyte in this case contained 10 cc. of manganese sulphate, containing 0.1034 gram of manganese, 5 cc. formic acid, and 1 gram of chrome alum. The current strength was 1.0 ampere with a pressure between the electrodes of 7.0 volts in the beginning to 5.5 volts at the end. The results obtained were, however, very unsatisfactory. The manganese was not all out in seven and three-fourths hours, instead of two and one-half hours without chrome alum. The current was then reduced to 0.08 ampere and the experiment run over night. The weight of the deposit of protosesquioxide of manganese gave 0.1500 of manganese instead of 0.1551 gram. Metallic specks were visible on the kathode and also in the deposit immediately below the kathode, where they had evidently fallen down from the kathode. A test of the deposit on the kathode showed the presence of chromium. Chrome alum as an addition to this electrolyte was therefore shown to be out of the question.

Recapitulating the results so far obtained, the following conclusions may be arrived at:

1. The statement of Kaeppel, that it is not possible to precipitate manganese completely in the presence of formic acid and that more than 5 drops of this acid prevent the deposition of the peroxide of manganese entirely, is not born out by the experi-

mental facts, obtained under the conditions described above. It is evident, therefore, that the conditions under which he performed his experiments must have been different, and it is a cause for regret that he did not publish them, as some interesting comparisons might then be made.

2. It is possible to obtain the deposit of peroxide from a formic acid solution in a beautifully adherent and satisfactory form, which can be washed and ignited without any trouble. Even the ignition has no tendency to loosen the deposit. The deposits up to 0.2851 of Mn_3O_4 do not show any tendency to scale off. This tendency, however, manifests itself when the manganese content of the solution is higher, but even then it is very small.

3. Formic acid is a better electrolyte than acetic acid, it being only possible, according to Classen's statement cited above, to deposit 0.08 gram of manganese in the form of peroxide.

As it was thus ascertained that the deposition of manganese could be performed easily and satisfactorily in an electrolyte which contained formic acid, the question arose as to whether it would also be possible to effect the separation of manganese from other metals and especially from iron. The latter had not been satisfactorily accomplished at all up to the present time, as will appear from the following quotations: Neumann[1] says in regard to the separation of iron and manganese: "A great number of experiments have been carried out with all forms of salts in order to discover a reliable method for obtaining a complete separation of these two metals, but without success. In most of these experiments the aim has been to obtain the manganese as peroxide at the anode or to keep it in solution, while the iron is deposited at the kathode. The results obtained showed that the deposition of the iron was incomplete (at least for the first deposition), and that when the manganese was separated as peroxide, this latter contained iron.

This difficulty arises in connection with the method proposed by Classen.[2] The solution of the two metals is prepared by treating it with 6 or 8 grams of ammonium oxalate, and after heating to 50° or 60° C. the electrolysis is conducted with a current of 1

[1] "The Theory and Practice of Electrolytic Methods of Analysis," translated by Kershaw, London, 1898.

[2] Electrolysis.

ampere in density and of 3.1 to 3.8 volts as regards electromotive force. Only a small portion of the manganese is obtained at the anode as peroxide under these conditions. If less ammonium oxalate be used, permanganic acid and its salts will be formed at first at the anode and later a peroxide deposit will be obtained containing iron. As a rule, the liquid is rendered completely turbid by a brown flocculent precipitate, which partly settles in adherent form upon the kathode. The method gives inexact results in spite of all assertions to the contrary.

The method proposed by Brand,[1] in which a solution containing sodium pyrophosphate and ammonium oxalate and ammonium oxalate is used, also yields inaccurate results.

If one attempt to effect the separation of iron from manganese in a solution containing 20 to 30 grams of ammonium acetate an incomplete deposition of the manganese as peroxide occurs, owing to the formation of a ferrous salt, which dissolves the peroxide again at the anode. Engels[2] has proposed to use oxidizing agents in order to overcome this difficulty. If chromic acid be used to oxidize the ferrous salt a complete deposition of the manganese as peroxide can be obtained, but the deposit will be found to contain up to 0.02 gram iron, probably in the form of oxide."

Classen[3] says: "The hope that manganese in the presence of iron might be separated and determined in an acetic acid solution has not been fulfilled. Innumerable experiments, conducted under the most varied conditions and with the most diverse substances, have given no satisfactory results. In view of the great importance which a method for the direct determination of manganese in the presence of iron, etc., would possess, this investigation will be continued." Nothing further has been published by Classen up to now on this subject, consequently it must not have been possible to make the method work.

Kaeppel, in his paper repeatedly referred to, publishes also a method for the separation of iron and manganese. His acetone method had failed completely to give satisfactory results. He prepares his electrolyte by bringing a solution of 12 grams of sodium pyrophosphate to boiling, and adding, while stirring, a solution of ferrous ammonium sulphate and manganese ammo-

[1] Ztschr. anal. Chem., **28**, 581.
[2] Ztschr. Electrochemie, **2**, 414.
[3] Electrolysis, p. 149.

nium sulphate. After the solution has become clear he adds 5 drops of phosphoric acid. If a turbidity is caused by the addition of the phosphoric acid the solution is clarified again by the addition of a few drops of sodium pyrophosphate solution. The metallic salt solutions contained 0.1 to 0.15 gram of iron and 0.035 to 0.11 gram of manganese. The deposition of the iron takes eight and one-half to nine and one-half hours, and it is not possible to determine the manganese electrolytically in the solution after the iron is out. Electrolysis takes place at a temperature of 30° to 40° C.

It was therefore an interesting question whether it was possible to find a solution in which the iron and manganese could be separated. As the manganese peroxide deposits on the anode and the iron on the kathode it should be theoretically possible to obtain both of them at the same time. The beautiful character of the deposits obtained by the use of formic acid gave rise to the hope that it might be easily possible to separate the two metals in such a solution. Before going to this separation, however, the method was first tried on the separation of zinc and manganese. A solution of zinc sulphate, containing a calculated amount of 0.1 gram of metal in 10 cc., was used. Electrolysis was carried out in the usual manner, a roughened platinum dish serving as anode, while the platinum basket electrode was connected as kathode. It was found that the deposit of zinc showed an extreme tendency to come down in spots upon the kathode, and the basket electrode had to be carefully adjusted so that it was equidistant from the sides of the dish. It was also found that in this case the addition of ammonium formate seemed to exert beneficial influence on the character of the zinc deposit, the best results being obtained with a solution containing 10 cc. of a manganese sulphate solution with 0.1034 gram of manganese, 10 cc. zinc sulphate solution with 0.1000 gram of zinc, 10 cc. of formic acid of 1.06 specific gravity and 5 cc. of a solution of ammonium formate obtained by neutralizing 1.06 specific gravity formic acid by ammonia. The following table shows some of the results obtained:

Mn present.	Mn found.	Zn present.	Zn found.	Time. Hours.	Temperature.	$N.D._{100}$ anode.	$N.D._{100}$ kathode.	Voltage.
0.1034	0.1037	0.1000	0.0998	11	ordinary	1.0	1.66	5.4
0.1034	0.1033	0.1000	0.01001	11½	"	1.0	1.66	5.4
0.1034	0.1036	0.1000	0.01003	11	"	1.0	1.66	5.4

After this question had been satisfactorily solved, the chances seemed to be very promising that iron might be easily separated from manganese in a formic acid solution. But these hopes seemed to be doomed to disappointment, for when a separation was tried under the conditions which had proved most successful for manganese alone, not much of a result was obtained, even if electrolysis was continued for twelve hours. The electrolyte in that case consisted of 10 cc. of a ferric ammonium sulphate solution, containing 0.1000 gram of metallic iron, 10 cc. manganese sulphate, containing 0.1034 gram manganese and 5 cc. formic acid. The basket electrode served as kathode and the dish as anode. A long series of experiments were then started in order to ascertain the best conditions for a separation. It was first tried to obtain a better result by varying the amount of formic acid in the solution. It was found that 10 cc. of the acid, with the same amount of iron and manganese present as above, gave the best results, but they were still far from quantitative. In order to ascertain whether the substitution of a ferrous sulphate solution for the ferric ammonium sulphate solution would prove beneficial, electrolytes were tried, containing $FeSO_4$, but the results obtained were still less encouraging than those gotten before. It was thought that various current densities at the anode, as well as at the kathode, might have an influence on the result and perhaps bring more success. Accordingly, the current density was varied at the anode from $N.D._{100} = 0.15$ to $N.D._{100} = 2.8$. The current density at the kathode was also varied from $N.D._{100} = 0.15$ to 47 by using spiral, basket and gauze electrodes, but the result was unsatisfactory. It was also tried to see whether a uniform current density at the electrodes would prove beneficial, and therefore a number of experiments were made by introducing the solution into a beaker glass and suspending into it two platinum gauze electrodes, arranged exactly opposite each other. This was again unsuccessful, for not only was it impossible to get the two metals out completely, but at the edge of the kathode there formed a small deposit, consisting of a brown colored manganese compound, as was ascertained by scraping some of it off and testing it. It was noticed in all of this work that, in order to obtain the iron free from manganese, it was absolutely essential to have the current density at the kathode entirely uniform, that is to say, all parts of the kathode had to be equidistant from the anode surface.

If there was one point of the kathode nearer to the anode there was danger of some oxide of manganese depositing there. Perhaps this fact is an explanation why it has not been possible to obtain concordant results with methods proposed up to the present time, when they were worked by different investigators.

Electrodes of sheet platinum were also tried. The results from all these trials were disappointing, for, though the separation of the two metals could be effected, one metal not containing any of the other, yet it was impossible to get all of the metals out of the solution even in periods varying from eleven to twelve hours.

As the addition of ammonium formate had proved beneficial in the case of zinc, experiments were also carried out with the addition of varying amounts, from 1 to 15 cc., obtained by neutralizing formic acid of 1.06 specific gravity with ammonia, to varying amounts of formic acid, from 5 to 20 cc. 1.06 specific gravity. Its presence in small quantity was found to have a beneficial effect, as a greater amount of iron was obtained, but it was not possible to get all the iron out even when the electrolysis was continued for more than twelve hours. Additions of formaldehyde, in small quantity, were found to retard the precipitation of manganese, though they had no effect upon accelerating the deposition of iron.

It was then decided to see whether it was not possible to separate the two metals by retarding or preventing the deposition of peroxide of manganese altogether. Accordingly, the use of formic acid was abandoned for the time being, and as experiments had proved that in an electrolyte of tartaric acid the manganese was almost completely held up, it was decided to try this acid in conjunction with formaldehyde, which had also been found to have a retardent effect on the manganese. As ammonium formate had been found to have a beneficial effect on the deposition of the iron, it was used in conjunction with the other two. In order to obtain as high a conductivity of the solution as possible and to get along with as small a voltage as possible and yet obtain the high current strength necessary for precipitating the iron, an addition of 3 grams of ammonium sulphate was made to the electrolyte. This finally led to the desired result. In an electrolyte of this kind a complete and thorough separation of the iron and manganese could be effected. Electrolysis was conducted in the following manner: The electrolyte contained 10 cc. of man-

ganese sulphate solution, containing 0.1034 gram of manganese, and 10 cc. of a ferric ammonium sulphate solution containing 0.1003 gram of iron. To this were added 10 cc. of a ammonium formate solution, made as described above, by neutralizing 1.06 specific gravity acid by ammonia, and 10 cc. of an ammonium sulphate solution containing 3 grams of this salt. 1 cc. of a solution of 45 per cent. formaldehyde was also added. The platinum dish was used as kathode, and the basket electrode, which had been used before, was introduced as anode. The basket electrode was chosen in order to provide as much anode surface as possible for the deposition of any manganese peroxide which might be deposited there, and thus assure its adhering to the anode. The solution was then made up to 130 cc., in order to cover as nearly as possible 100 sq. cm. of the dish. Electrolysis was conducted in the cold, with a voltage between electrodes of 3.5 volts and an amperage of 1.4 amperes, the $N.D._{100}$ at the anode being consequently 2.33 and at the kathode 1.4. The iron deposited in from three to five hours in a beautiful form, and not a trace of it could be detected in the solution. The deposit, when tested, also proved to be entirely free from manganese. A little bit of peroxide of manganese precipitated on the anode in a beautifully adherent form, but only from 0.0055 to 0.006 gram of peroxide had deposited at the end of the electrolysis when the iron was all out. No peroxide was swimming in the electrolyte and the solution was colored red from the permanganic acid formed. It was soon found, however, that the deposit of iron could not be weighed, as it contained varying and sometimes considerable amounts of carbon. The odor of hydrocarbons was quite perceptible on dissolving the deposited metal in dilute sulphuric acid, and a residue was left on the dish after this operation, which could be volatilised by igniting the dish. This carbon content proved, however, no obstacle to a successful determination of the iron, as it was easily possible to dissolve the deposit of the dish very quickly by introducing some distilled water and a few cc. of concentrated sulphuric acid. The solution was then transferred to a beaker and boiled for a few minutes in order to get rid of the hydrocarbons. A little granulated zinc was then added in order to reduce any iron which might have become oxidized, and the solution was then titrated with a very dilute standardized solution of potassium permanganate. The whole manipulation in this way

consumed perhaps less time than the drying and weighing of the dish would have done. The following table gives the results of a number of experiments, run in the way above described.

The solution, when taken off, had a fishy smell, due to decomposition products of the formaldehyde. The addition of the latter was discontinued after it had been shown by experiments that its presence had no influence on the result. The fishy smell of the solution did not appear any more after formaldehyde was no longer used. Results with and without formaldehyde are given in the above table.

Though it was shown by these experiments that in an electrolyte composed as above, a successful separation of the iron and manganese could be accomplished in much less time than by the method of Kaeppel, as cited above, and a method, which would also work in the presence of a large amount of manganese, yet it was felt that only half the problem had been solved in this way. The fact that the manganese could not be determined electrolytically after the iron was all out, and anyway, the fact that it had to be held up and thus prevented from deposition, were sufficient stimulants to renew the effort of finding a method by which the two metals could be determined simultaneously. It was felt that the experiments with formic acid had given considerable encouragement, and all that was needed was to find some addition to the electrolyte for the purpose of accelerating the deposition. Accordingly, the experiments with formic acid were resumed.

The electrolyte, which had been found most favorable formerly, contained 10 cc. of manganese sulphate, 10 cc. of ferric ammonium sulphate and 10 cc. formic acid of 1.06 specific gravity. The desired result was first thought might be obtained by the use of an oxidizing agent. As such nitric acid was chosen, and various additions, from 10 drops to 10 cc. of concentrated acid were made. It was found, however, that this had the effect of preventing the deposition of iron altogether and that of manganese to a large extent. It was therefore abandoned and the addition of a reducing substance tried. Sodium sulphite was chosen as such, and ¼ gram of it added to the solution. This had the effect of bringing out the deposit of peroxide of manganese in shorter time than before, and a very fine deposit of iron, but in six and one-half hours neither all the iron nor all the manganese was out

Iron present.	Iron found.	Manganese present.	Tartaric acid. Grams.	Ammonium formate. cc.	Formaldehyde 45 per cent. cc.	Ammonium sulphate. Grams.	Time.	Temp.	$N.D._{100}$.	Voltage.
0.1003	0.1001	0.1034	1	10	1	3	4	ordinary	1.4	3.5
0.1003	0.1003	0.1034	1	10	1	3	4½	"	1.4	3.5
0.1003	0.0999	0.1034	1	10	1	3	3½	"	1.4	3.5
0.1003	0.0999	0.1034	1	10	1	3	4	"	1.4	3.5
0.1003	0.1001	0.1034	1	10	1	3	4	"	1.4	3.5
0.1003	0.1001	0.1034	1	10	1	3	4	"	1.4	3.5
0.0982	0.0982	0.1034	1	10	1	3	4	"	1.4	3.5
0.0982	0.0983	0.1034	1	10	none	3	4	"	1.4	3.5
0.0982	0.0982	0.1034	1	10	none	3	4	"	1.4	3.5
0.0982	0.0978	0.1034	1	10	1	3	4	"	1.4	3.5
0.0982	0.0980	0.1034	1	10	1	3	4	"	1.4	3.5

of the solution. A larger amount of sodium sulphite was evidently needed, but when ½ gram of it was introduced into the solution the salt was itself decomposed under the action of the current, with a liberation of sulphur all through the electrolyte. As it was considered undesirable to have this precipitate of sulphur in the solution, as it might contaminate the deposits and interfere with the results, it was then tried to add the sodium sulphite at intervals during electrolysis, $^1/_{10}$ gram at a time. This was carried out and was soon found to be effective in removing the iron. Electrolysis was carried out as usual in the roughened platinum dish with the basket platinum electrode, it having been found by repeated trials that a spiral kathode could not be used, as there was invariably a precipitate of oxide of manganese on it, especially on he outer rim, which was nearest to the anode. This was evidently due to a high current density at the kathode and was in line with observations mentioned above. The electrolyte was made up in such a manner that 10 cc. of a solution, containing $^1/_{10}$ gram of sodium sulphite, were introduced into the dish and the ferric ammonium sulphate, 10 cc. containing 0.0997 gram of iron, was added. The solution immediately acquired a very dark red color. The usual 10 cc. of $MnSO_4$ were then added, and after that the formic acid solution. 5 cc. of formic acid of 1.06 specific gravity were found to answer well. It was found that the addition of 1 cc. of a sodium sulphite solution, containing $^1/_{10}$ gram in 1 cc. for every half hour at the beginning for 2 times, and an addition of an equal amount every hour until the iron was out, answered well. A very good indication of the gradual deposition of the iron is furnished by the fact that on each addition of sodium sulphite the color of the solution deepens quite perceptibly, the coloring getting weaker, the less iron is present. When only traces of iron are left in the solution it does not color any more on the addition of sodium sulphite. It has then to be watched and tested for iron from time to time, until no reaction is obtained any more. Care must be taken in this connection that the electrode with the iron deposit on it be taken out as soon as no reaction for iron can be obtained. If that is not done there is danger of some of the iron going into solution again if left too long. The basket electrode is then removed, washed off and an auxiliary spiral electrode inserted as quickly as possible

into the solution in order to prevent the peroxide of manganese, which has precipitated, from dissolving in the electrolyte. Care must be taken during the time that this spiral electrode is in the solution, to insert resistance into the circuit, so as to cut down the current to 0.1 ampere or less, in order to prevent anything from precipitating on the spiral electrode. If this precaution be not taken there will invariably be a brown-looking deposit on the electrode. The basket electrode with the deposit of iron on it is introduced into a small beaker and covered with distilled water. A few cc. of concentrated sulphuric acid are then added and the solution of the iron will take place rapidly. The basket is then washed off and reintroduced into the electrolyte, after the spiral electrode has been taken out. 5 cc. of formic acid of 1.06 specific gravity is then added, and the current raised to its original value again for the purpose of precipitating the rest of the manganese. A little granulated zinc is then introduced into the iron solution for the purpose of reducing any of the metal which has oxidized during the time that the auxiliary kathode was introduced, and the iron is then titrated in the usual manner. It is not possible to obtain the iron by weighing, for, though a fine looking deposit is obtained, there is invariably some slight oxidation during the time necessary to change electrodes. The results obtained are shown in the following table and are very satisfactory and concordant.

Fe present.	Fe found.	Mn present.	Formic acid 1.06. cc.	Sodium sulphite.	Time.	Temp.	N.D.$_{100}$ kathode.	Voltage.
0.1010	0.1008	0.0988	5	6 additions $^1/_{10}$ gm. each	$4^1/_2$	ordinary	1.2	4.4
0.1010	0.1008	0.0988	5	"	5	"	1.2	4.4
0.1010	0.1010	0.0988	5	"	5	"	1.2	4.4
0.1010	0.1008	0.0988	5	"	5	"	1.2	4.4
0.1010	0.1011	0.0494	5	"	$4^1/_2$	"	1.2	4.4
0.1010	0.1007	0.0494	5	"	$4^1/_2$	"	1.2	4.4
0.1010	0.1010	0.0494	5	"	5	"	1.2	4.4
0.1010	0.1009	0.0988	5	"	5	"	1.2	4.4
0.1010	0.1011	0.0988	5	"	5	"	1.2	4.4
0.1010	0.1007	0.0988	5	"	5	"	1.2	4.4
0.1010	0.1011	0.0988	5	"	5	"	1.2	4.4

It was thus establshed that the separation of iron and manganese could also be effected in an electrolyte, consisting mainly of formic acid. It was found, however, that though the sodium

sulphite was very effective as far as the iron was concerned, it acted as a retarding agent upon the manganese, inasmuch as it was found impossible to remove the last traces of manganese in any reasonable time. When only 0.0494 gram of manganese were present, the complete deposition could be effected in about ten to eleven hours, but thirteen or fourteen hours were needed for 0.0988 gram of manganese. The precipitate obtained at the end of electrolysis, when all the manganese was deposited, was not adherent, though at the time when the electrode with the iron deposit on it was removed the deposit of manganese peroxide appeared adherent. This was probably due to the action of the large amount of gas set free at the anode, as the electrolysis had to be continued such a long time in order to bring out the last traces of the manganese. However, this fact of the precipitate being loose, was not considered very much of a drawback, as the experiments mentioned in the beginning had shown that the presence of a sodium compound in the electrolyte was not desirable when the precipitate of manganese peroxide was adherent. The precipitate, moreover, was scaly and very heavy, and settled rapidly down to the bottom of the beaker, to which the siphoned-off solution was transferred. The solution in these, as in all other experiments was replaced by distilled water, while the current was still running, and the current then interrupted. As the precipitate settled down to the bottom, the supernatant liquid could be almost entirely decanted off and the precipitate filtered quickly and washed thoroughly. The washing was performed with hot water and continued for some time, in order to remove any alkali which might be present. The filter was then dried, the precipitate brushed into the dish, the filter burned separately and the ashes added to the material in the dish, after which the dish was ignited in the usual manner. The results obtained were very satisfactory as far as separation is concerned, as is shown by the following table:

Fe present.	Fe found.	Mn present.	Mn found.	Formic acid 1.06.	Sodium sulphite.	Time.	Temperature.	$N.D._{100}$ anode.	$N.D._{100}$ kathode.	Voltage.
0.1010	0.1011	0.0494	0.0499	5	6 instalments $\frac{1}{10}$ gm. each.	10	ordinary.	2.0	1.2	4.4
0.1010	0.1007	0.0494	0.0497	5	"	11½	"	2.0	1.2	4.4
0.1010	0.1010	0.0494	0.0497	5	"	11	"	2.0	1.2	4.4
0.1010	0.1008	0.0988	0.0990	5	"	12½	"	2.0	1.2	4.4
0.1010	0.1008	0.0988	0.0994	5	"	14	"	2.0	1.2	4.4
0.1010	0.1010	0.0988	0.0987	5	"	14	"	2.0	1.2	4.4
0.1010	0.1011	0.0988	0.0992	5	"	14	"	2.0	1.2	4.4

The problem of the separation of the iron and manganese and the electrolytic determination of manganese in the same solution had thus been solved, but unfortunately the time required was very long and probably too long to make the method of practical value. The next experiments were therefore undertaken with a view to reduce the time necessary for the complete precipitation of the manganese, after the iron was out. Various means were adopted to accomplish this, the first being, as would naturally suggest itself from the usual practice, to raise the current in order to get the last traces out. It was soon found, however, that this method did not work in this case, and that there was danger, if the current was raised above 1.4 amperes, that some manganese compound would precipitate on the kathode. This would take place to a considerable degree if the current was raised to 2 amperes, corresponding to a current density at the kathode of $N.D._{100} = 3.3$, an at the anode of $N.D._{100} = 1.6$ to 2

Varying amounts of ammonium formate were then introduced, but did not prove beneficial. Additions of hydrogen peroxide up to 10 cc. of a 3 per cent. solution also did not improve matters, for while they evidently had some action on the deposit, in making it more adherent, yet the last traces of the manganese did not come out any faster, but rather the reverse. Additions of alcohol in quantities up to 10 cc. and of acetone of 5 and 10 cc. did not have a beneficial effect. Considerable time was thus spent in trying to reduce the time for the precipitation of manganese, but no headway could be made.

It was then decided to see whether ammonium acetate would prove of value in this connection and a solution was made by

neutralizing ordinary acetic acid of 1.06 specific gravity with ammonia, to a barely acid reaction. An experiment was run in the usual manner with addition of sodium sulphite, until the iron was out and removed. Ten cc. of the ammonium acetate solution were then added and the electrolysis continued. The result was quite surprising, for after two hours the level of the solution was raised and it was observed that no manganese peroxide deposited any more. When the solution was tested, no manganese was found to be present. The time of deposition of the peroxide had thus already been cut down from thirteen or fourteen hours to seven hours. The deposit weighed 0.0992 gram while 0.0988 was present.

As it was felt that the presence of sodium sulphite in the electrolyte was not altogether desirable and that it would be better, in order to remove all possible sources of error, if the separation could be effected without introducing it, the next endeavor was made in the direction of reducing its quantity. Incidentally it was also desirable to cut down the time required for the deposition of the iron and to do away with the necessity of removing the basket electrode, after the iron had all deposited on it, in order to prevent any re-solution. Accordingly ammonium acetate was introduced from the start and the quantity of sodium sulphite was cut down to 3 cc. = 0.3 gram and 2 cc. = 0.2 gram. For precaution's sake the basket electrode, with the major part of the iron on it, was also removed, but it was found that 93 per cent. of the iron had already deposited in two hours, and the rest was found when the electrode was removed at the end of the electrolysis. The surprising result was found that the iron and manganese were all out of the solution at the end of four hours. The iron was titrated as usual and the manganese peroxide filtered off and the results agreed very closely with the amounts present in the solution. It was then tried to reduce the quantity of sodium sulphite still further and to add only 10 drops, corresponding to only 0.05 gram of the salt. It was found, that the separation could be effected just as satisfactorily as before, and that the electrode with the deposit of iron on it, did not have to be removed from the solution. The complete deposition of the two metals was again accomplished in four hours. The next step was then to try and get along without the sodium sulphite altogether and it was finally ascertained that if was not

necessary to add any of it. The separation took place just as well in formic acid solution, to which only ammonium acetate had been added. However, as had already been noted in the beginning of these experiments and mentioned there in connection with the use of sodium formate, the sodium salts seem to have an accelerating effect upon the precipitation of the manganese. Just in the same manner as the deposition of peroxide of manganese in formic acid solution took place more quickly when sodium formate was present, than without it, so in this case the complete precipitation is from one-half to one hour slower without than with, even as little as 10 drops or 0.05 gram of sodium sulphite. Still without its use there is no danger of any deleterious effect due to its presence, and the character of the deposit of peroxide shows a decided improvement, it being almost entirely adherent. Only a trifle came off during the washing and this small amount could easily be collected on a small filter and added to the deposit in the dish. The final experiments were run in the following manner: 10 cc. of manganese sulphate solution containing 0.0988 gram of manganese were introduced into the roughened platinum dish, and 10 cc. of ferric ammonium sulphate solution contaning 0.0996 of iron were added. Then 5 cc. of formic acid of 1.06 specific gravity and 10 cc. of an ammonium acetate solution, obtained by neutralizing 1.06 specific gravity acetic acid by ordinary chemically-pure ammonia to barely acid reaction, were added, the basket electrode introduced and a current of 1.1 amperes, with a pressure of 3.9 volts between the electrodes, was allowed to act for five hours. At the end of this time the level of the solution was raised, and no further precipitation took place. The solution was then siphoned off as before, both of the electrodes washed carefully and the iron titrated in the usual manner, while the manganese peroxide, after the small amount of loose material had been filtered off and added to the material in the dish, was ignited and weighed in the usual manner. The following table shows the close agreement of the results obtained: